NATO LECTURES

M. Meyyappan

Introduction to Nanotechnology

Abstract

Nanotechnology deals with creation of materials, devices and systems in the nanometer scale (1-100 nm) through manipulating matter at that scale and exploiting novel properties arising because of the nanoscale. This lecture will first define nanotechnology, particularly describing what it is and what it is not, followed by detailed examples of change in various properties seen by going from bulk to nanoscale. The effect of nanoscale on physical properties, bandgap, etc. will be illustrated. Examples of novel nanomaterials such as nanotubes, nanowires, nanoparticles, etc. will be introduced. Also, the tools used in nanotechnology research such as the scanning probe microscopes, scanning tunneling microscopes etc. will be mentioned and a summary of top-down and bottom-up processes needed in manufacturing will be presented as an introduction to the more detailed coverage later. Finally, a broad overview of the potential of nanotechnology on a sector-by-sector basis will be given to set the stage for the subsequent lectures in this NATO series.

Nanotechnology deals with creation of materials, devices and systems through manipulation of matter at the nanometer length scale. The object created itself does not have to be nanoscale, but can be micro or macro size. What is critical is the ability to exploit the novel properties that arise because of nanometer length scale. Indeed when we go down from bulk to nanoscale, physical, chemical, mechanical, electrical, optical, magnetic and other properties change. The field is about making use of such changes and developing novel products and processes which have not been possible until now.

Meyyappan, M. (2007) Introduction to Nanotechnology. In *Nanotechnology Aerospace Applications – 2006* (pp. 1-1 – 1-2). Educational Notes RTO-EN-AVT-129bis, Paper 1. Neuilly-sur-Seine, France: RTO. Available from: http://www.rto.nato.int/abstracts.asp.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **01 MAR 2007**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**
4. TITLE AND SUBTITLE **Introduction to Nanotechnology**		5a. CONTRACT NUMBER
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)		5d. PROJECT NUMBER
		5e. TASK NUMBER
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **MM Associates Mail stop 229-3 Bldg 229, Room 214 Moffett Field, CA 94035 UNITED STATES**		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release, distribution unlimited**		
13. SUPPLEMENTARY NOTES **See also ADM002060., The original document contains color images.**		
14. ABSTRACT		
15. SUBJECT TERMS		

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**SAR**	**41**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

The advent of scanning tunneling microscope and atomic force microscope in the 1980s has essentially ushered in the nano era. With these powerful tools, scientists were able to see nature at the atomic level. Simultaneously, with increased computing power available, modeling and simulation enabled an understanding of properties at the nanoscale. This powerful combination of atomic scale characterization and detailed modeling has led to the explosion we see today in nanoscale science and technology research.

Nanoscale materials have a large surface area for a given volume. The surface properties dominate compared to bulk properties. Quantum phenomena becomes critical at reduced length scales. In most cases, the change in behavior is not a simple extrapolation of bulk behavior as we know. In materials where strong chemical bonding is present, delocation of valence electrons can be extensive. The extent of delocalization can vary with the size of the system. Structure also changes with the size. These two changes can lead to different physical and chemical properties depending on size, for example, magnetic, optical properties, melting point, specific heat, surface reactivity, bandgap, etc.

Nanomaterials currently under investigation include nanoparticles, nanotubes, nanowires, powders, quantum dots, nanoporous materials, dendrimers, nanofibers, fullerenes, etc. Examples of each of these will be discussed in the presentation. The application range for these materials is very broad from electronics, sensors, electromechanical systems to composites, coatings and lubricants.

Introduction to Nanotechnology

M. Meyyappan

Nanotechnology is the creation of **USEFUL/FUNCTIONAL** materials, devices and systems (of any useful size) through control/manipulation of matter on the nanometer length scale and exploitation of novel phenomena and properties which arise because of the nanometer length scale:

- Physical
- Chemical
- Electrical
- Mechanical
- Optical
- Magnetic
-
-

Nanometer

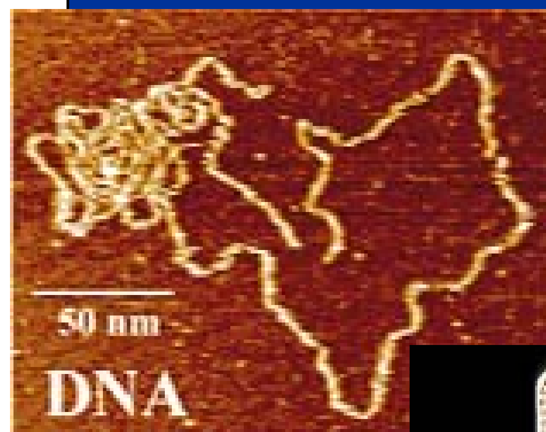
- One billionth (10^{-9}) of a meter
- Hydrogen atom 0.04 nm
- Proteins ~ 1-20 nm
- Feature size of computer chips 90 nm (in 2005)
- Diameter of human hair ~ 10 µm

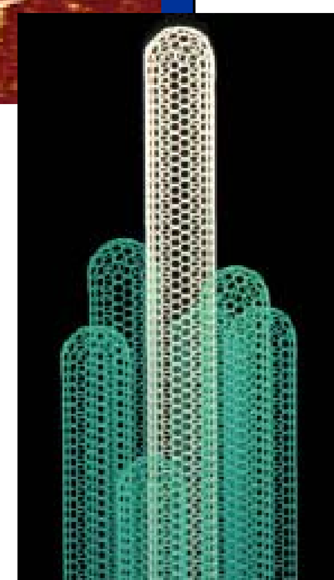
- Examples
  - Carbon Nanotubes
  - Proteins, DNA
  - Single electron transistors

- Not just size reduction but phenomena intrinsic to nanoscale
  - Size confinement
  - Dominance of interfacial phenomena
  - Quantum mechanics

- New behavior at nanoscale is not necessarily predictable from what we know at macroscales.

AFM Image of DNA





What is Special about Nanoscale?

- Atoms and molecules are generally less than a nm and we study them in chemistry. Condensed matter physics deals with solids with infinite array of bound atoms. Nanoscience deals with the in-between meso-world
- Quantum chemistry does not apply (although fundamental laws hold) and the systems are not large enough for classical laws of physics
- Size-dependent properties
- Surface to volume ratio
  - A 3 nm iron particle has 50% atoms on the surface
  - A 10 nm particle → 20% on the surface
  - A 30 nm particle → only 5% on the surface

What is new about Nanoscience?

- Many existing technologies already depend on nanoscale materials and processes
  - photography, catalysts are “old” examples
  - developed empirically decades ago
- In existing technologies using nanomaterials/processes, role of nanoscale phenomena not understood until recently; serendipitous discoveries
  - with understanding comes opportunities for improvement
- Ability to design more complex systems in the future is ahead
  - designer material that is hard and strong but low weight
  - self-healing materials

STM

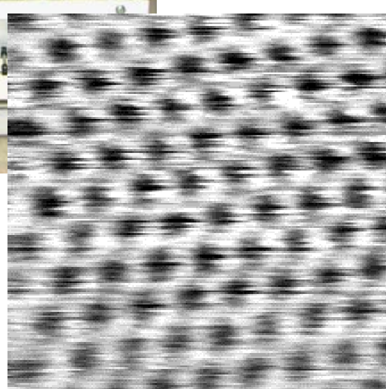


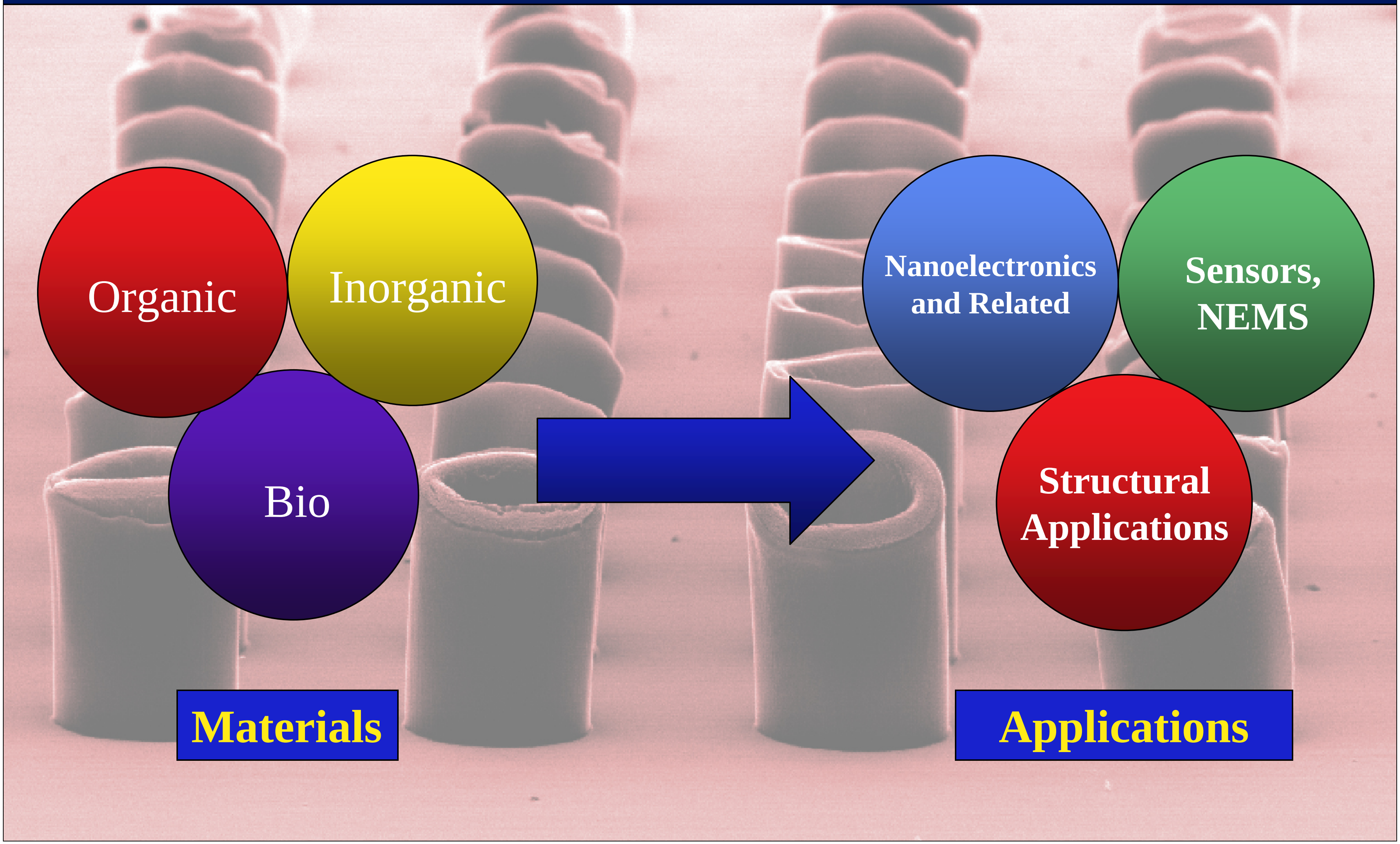
Image of Highly Oriented Pyrolitic Graphite

- 1959 Feynman Lecture *"There is Plenty of Room at the Bottom"* provided the vision of exciting new discoveries if one could fabricate materials/devices at the atomic/molecular scale.

- Emergence of instruments in the 1980s; STM, AFM providing the "eyes", "fingers" for nanoscale manipulation, measurement…

- Recently, there has been an explosion of research on the nanoscale behavior
  - Nanostructures through sub-micron self assembly creating entities from "bottom-up" instead of "top-down"
  - Characterization and applications
  - Highly sophisticated computer simulations to enhance understanding as well as create 'designer materials'

Nanotechnology R & D



Various Nanomaterials and Nanotechnologies

- Nanocrystalline materials
- Nanoparticles
- Nanocapsules
- Nanoporous materials
- Nanofibers
- Nanowires
- Fullerenes
- Nanotubes
- Nanosprings
- Nanobelts
- Dendrimers

- Molecular electronics
- Quantum dots
- NEMS, Nanofluidics
- Nanophotonics, Nano-optics
- Nanomagnetics
- Nanofabrication
- Nanolithography
- Nanomanufacturing
- Nanomedicine
- Nano-bio

As Recommended by the IWGN (Interagency Working Group on Nanotechnology) Panel

See www.nano.gov

- Nanostructure Properties
  - Biological, chemical, electronic, magnetic, optical, structural…
- Synthesis and Processing
  - Enable atomic and molecular control of material building blocks
  - Bioinspired, multifunctional, adaptive structures
  - Affordability at commercial levels
- Characterization and manipulation
  - New experimental tools to measure, control
  - New standards of measurement
- Modeling and simulation
- Device and System Concepts
  - Stimulate innovative applications to new technologies
- Application Development

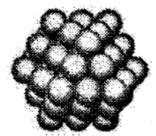
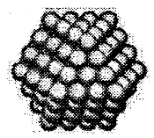
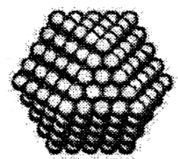
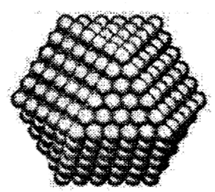
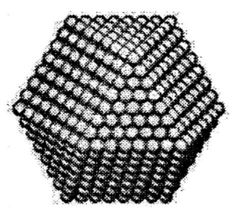
1. What novel quantum properties will be enabled by nanostructures (at room temp.)?
2. How different from bulk behavior?
3. What are the surface reconstructions and rearrangements of atoms in nanocrystals?
4. Can carbon nanotubes of specified length and helicity be synthesized as pure species? Heterojunctions in 1-D?
5. What new insights can we gain about polymer, biological…systems from the capability to examine single-molecule properties?
6. How can one use parallel self-assembly techniques to control relative arrangements of nanoscale components according to predesigned sequence?
7. Are there processes leading to economic preparation of nanostructures with control of size, shape… for applications?

This is NOT an exhaustive list

Some 'Nano' Definitions

- Cluster
  - A collection of units (atoms or reactive molecules) of up to about 50 units
- Colloids
  - A stable liquid phase containing particles in the 1-1000 nm range. A colloid particle is one such 1-1000 nm particle.
- Nanoparticle
  - A solid particle in the 1-100 nm range that could be noncrystalline, an aggregate of crystallites or a single crystallite
- Nanocrystal
  - A solid particle that is a single crystal in the nanometer range

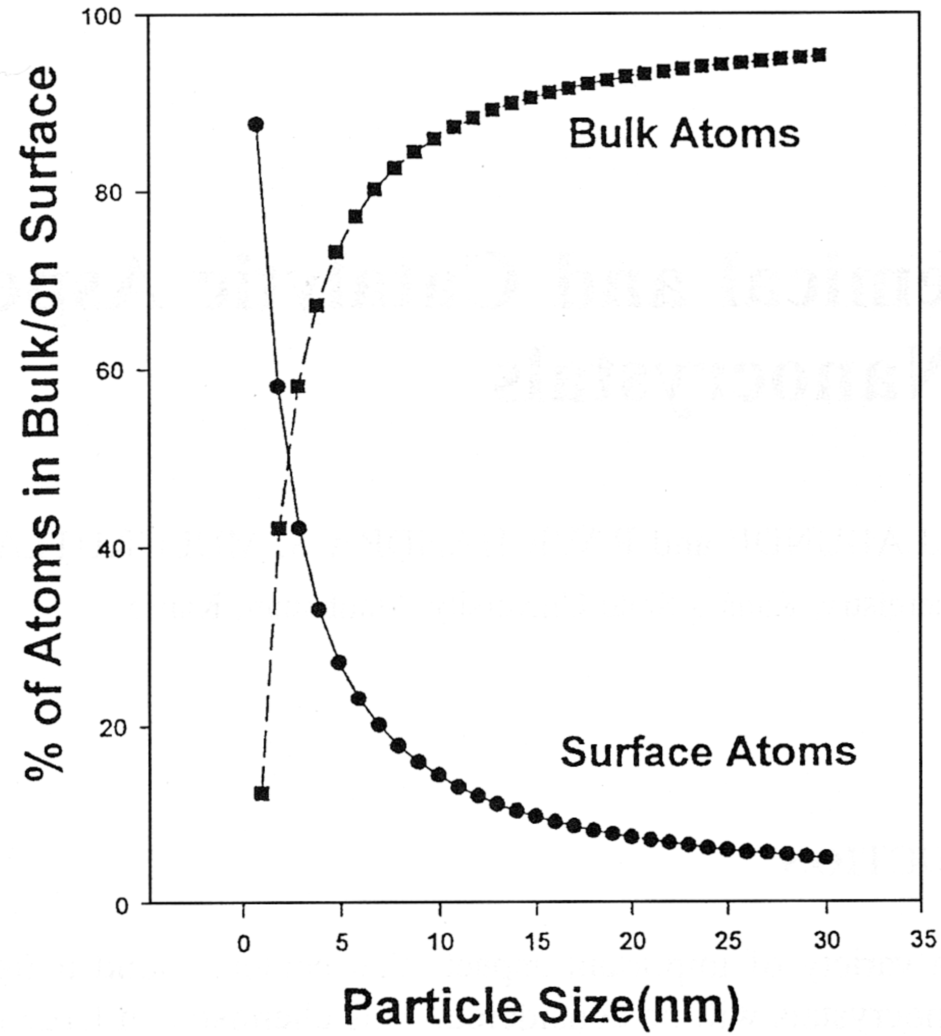
Percentage of Surface Atoms

Full-shell Clusters		Total Number of Atoms	Surface Atoms (%)
1 Shell		13	92
2 Shells		55	76
3 Shells		147	63
4 Shells		309	52
5 Shells		561	45
7 Shells		1415	35

Source: Nanoscale Materials in Chemistry, Wiley, 2001

Surface to Bulk Atom Ratio

- Spherical iron nanocrystals
- J. Phys. Chem. 1996, Vol. 100, p. 12142



Size Dependence of Properties

- In materials where strong chemical bonding is present, delocalization of valence electrons can be extensive. The extent of delocalization can vary with the size of the system.

- Structure also changes with size.

- The above two changes can lead to different physical and chemical properties, **depending on size**
  - Optical properties
  - Bandgap
  - Melting point
  - Specific heat
  - Surface reactivity
  -
  -

- Even when such nanoparticles are consolidated into macroscale solids, new properties of bulk materials are possible.
  - Example: enhanced plasticity

Some More Size-Dependent Properties

- For semiconductors such as ZnO, CdS, and Si, the bandgap changes with size
    - Bandgap is the energy needed to promote an electron from the valence band to the conduction band
    - When the bandgaps lie in the visible spectrum, changing bandgap with size means a change in color

- For magnetic materials such as Fe, Co, Ni, Fe_3O_4, etc., magnetic properties are size dependent
    - The ‘coercive force’ (or magnetic memory) needed to reverse an internal magnetic field within the particle is size dependent
    - The strength of a particle’s internal magnetic field can be size dependent

Color

- In a classical sense, color is caused by the partial absorption of light by electrons in matter, resulting in the visibility of the complementary part of the light
- On a smooth metal surface, light is totally reflected by the high density of electrons ⇒ no color, just a mirror-like appearance.
- Small particles absorb, leading to some color. This is a size dependent property.
  Example: Gold, which readily forms nanoparticles but not easily oxidized, exhibits different colors depending on particle size.
    - Gold colloids have been used since early days of glass making to color glasses. Ruby-glass contains finely dispersed gold-colloids.
    - Silver and copper also give attractive colors

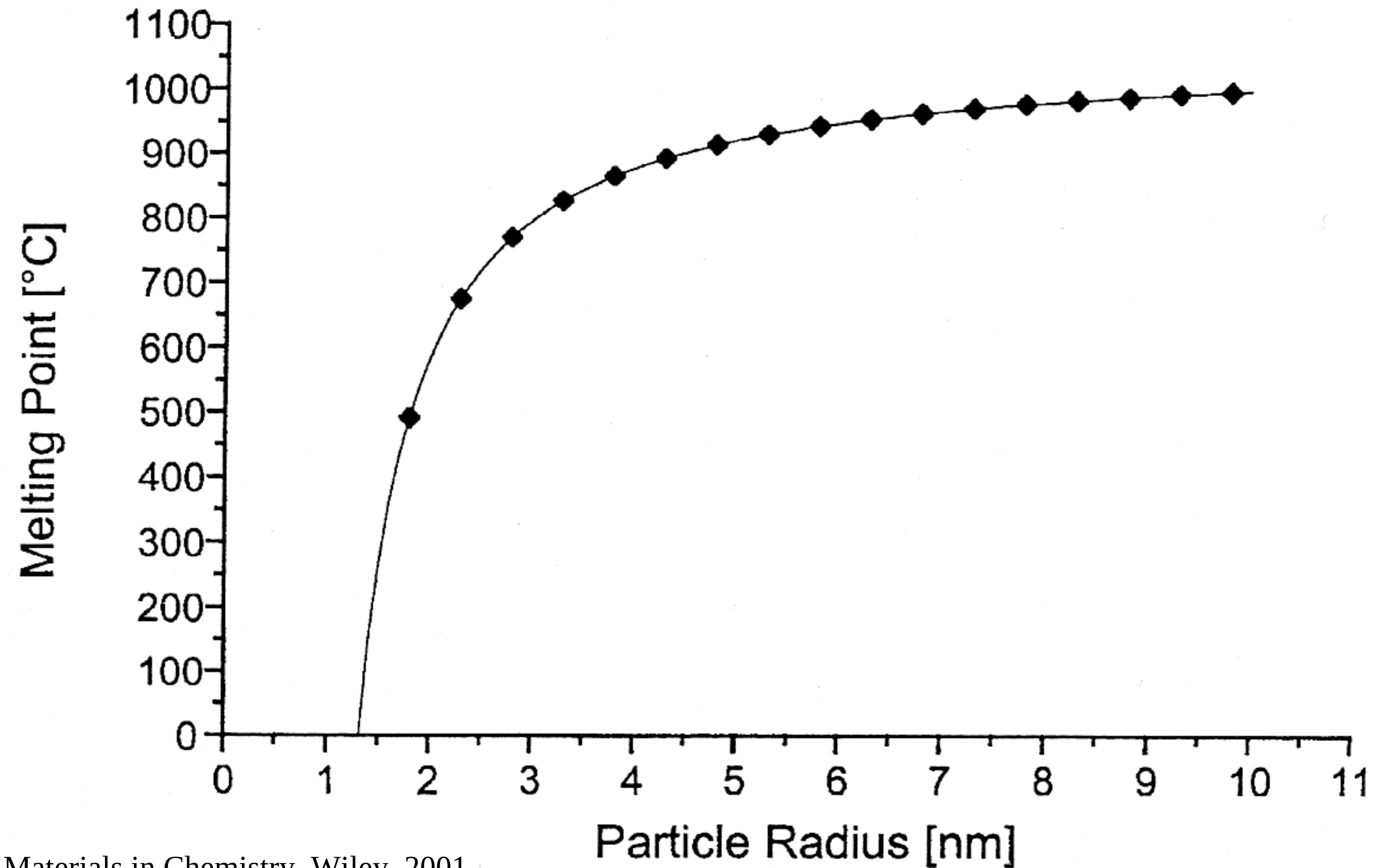
Specific Heat

- $C = \Delta Q/m\Delta T$; the amount of heat ΔQ required to raise the temperature by ΔT of a sample of mass m
- J/kg ·K or cal/g ·K; 1 calorie is the heat needed to raise the temp. of 1 g of water by 1 degree.
- Specific heat of polycrystalline materials given by Dulong-Petit law
  - C of solids at room temp. (in J/kg ·k) differ widely from one to another; but the molar values (in J/moles ·k) are nearly the same, approaching 26 J/mol ·K; $C_v = 3\ Rg/M$

    where M is molecular weight
- C_v of nanocrystalline materials are higher than their bulk counterparts. Example:
  - Pd: 48% ↑ from 25 to 37 J/mol.K at 250 K for 6 nm crystalline
  - Cu: 8.3% ↑ from 24 to 26 J/mol.K at 250 K for 8 nm
  - Ru: 22% ↑ from 23 to 28 J/mol.K at 250 K for 6 nm

Melting Point of Gold Particles

The melting point decreases dramatically as the particle size gets below 5 nm



Source: Nanoscale Materials in Chemistry, Wiley, 2001

Melting Point Dependence on Particle Size

- Lowering of the melting point is proportional to 1/r
- $\Delta\theta$ can be as large as couple of hundred degrees when the particle size gets below 10 nm!
- Most of the time, σ the surface tension coefficient is unknown; by measuring the melting point as a function of radius, σ can be estimated.
- Note: For nanoparticles embedded in a matrix, melting point may be lower or higher, depending on the strength of the interaction between the particle and matrix.

Electrical Conductivity

- For metals, conductivity is based on their band structure. If the conduction band is only partially occupied by electrons, they can move in all directions without resistance (provided there is a perfect metallic crystal lattice). They are not scattered by the regular building blocks, due to the wave character of the electrons.

$$\mu = \frac{e\lambda}{4\pi\varepsilon_o m_e v}$$

v = electron speed
ε_o = dielectric constant in vacuum

τ, mean time between collisions, is λ/v

- For Cu, $v = 1.6 \times 10^6$ m/s at room temp.; $\lambda = 43$ nm, $\tau = 2.7 \times 10^{-14}$ s

Electrical Conductivity (continued)

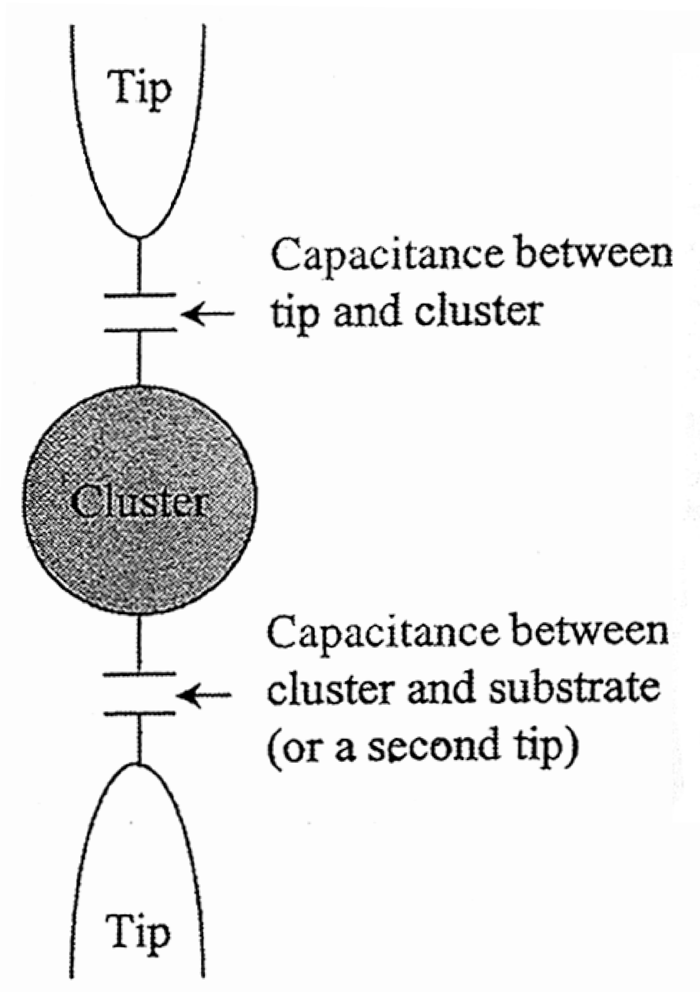
- Scattering mechanisms
  (1) By lattice defects (foreign atoms, vacancies, interstitial positions, grain boundaries, dislocations, stacking disorders)
  (2) Scattering at thermal vibration of the lattice (phonons)

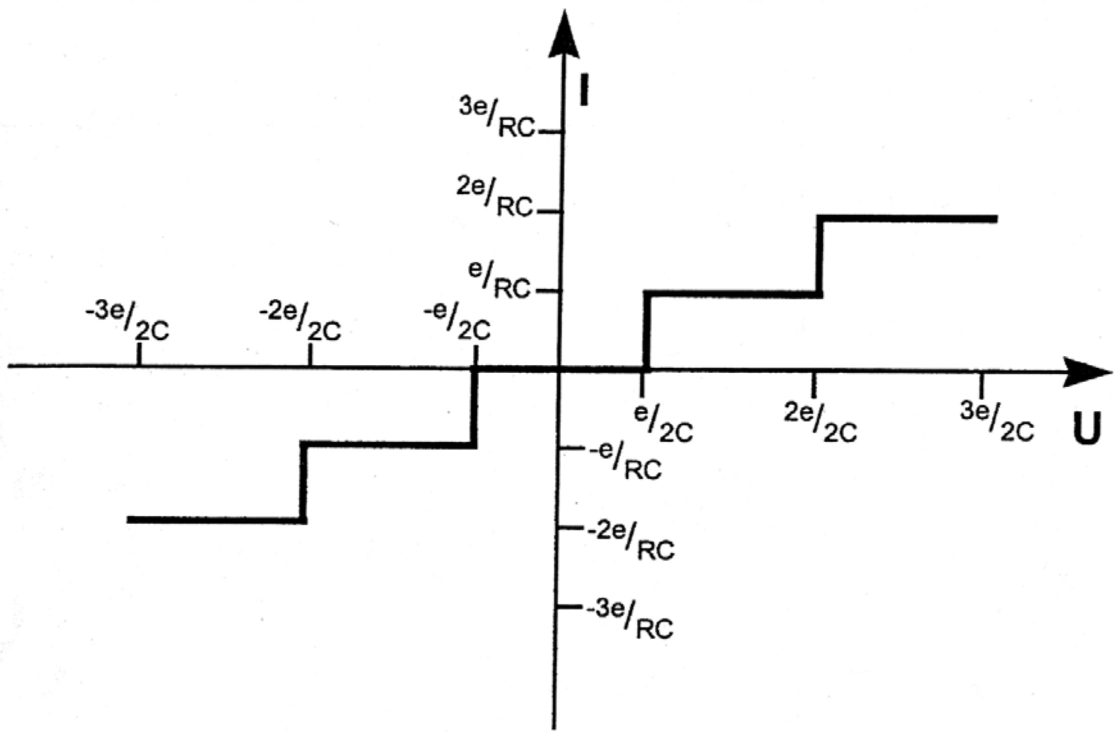
- Item (1) is more or less independent of temperature while item #2 is independent of lattice defects, but dependent on temperature.

- Electric current $\Rightarrow$ collective motion of electrons; in a bulk metal,
  Ohm's law: $V = RI$

- Band structure begins to change when metal particles become small. Discrete energy levels begin to dominate, and Ohm's law is no longer valid.

I-V of a Single Nanoparticle





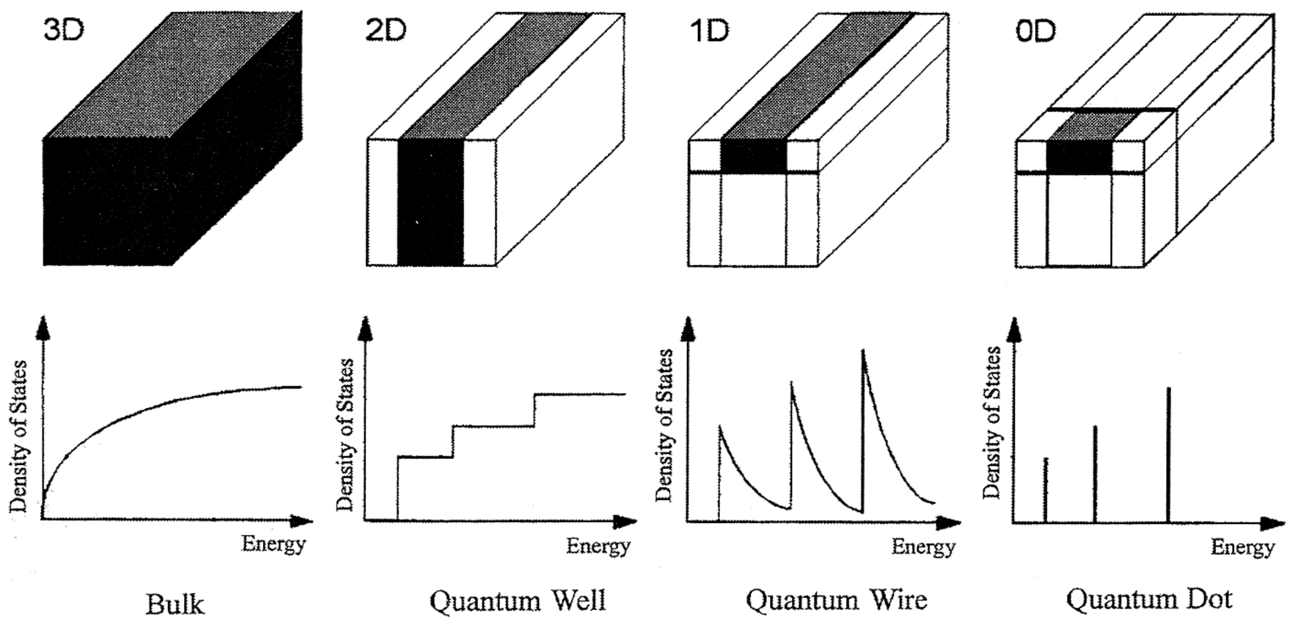
Source: Nanoscale Materials in Chemistry, Wiley, 2001

I-V of a Single Nanoparticle

- Consider a single nanoparticle between two electrodes, but cushioned by a capacitance on each side
  - If an electron is transferred to the particle, its coulomb energy ⬆ by
    $$E_c = e^2/2c$$
  - Thermal motion of the atoms in the particle can initiate a charge & E_c, leading to further electrons tunneling uncontrollably
  - So, $kT << e^2/2c$
  - Tunneling current $I = V/R_T$
  - Current begins at coulomb voltage $V_c = \pm e/2c$ which is called coulomb blockade
  - Further electron transfer happens if the coulomb energy of the 'quantum dot' is compensated by an external voltage $V_c = \pm ne/2c$ where n is an integer

- Repeated tunneling results in a 'staircase' with step height in current, e/Rc
- Possible to charge and discharge a quantum dot in a quantized manner ➡ principle behind some future computers

3D → 2D → 1D → 0D



Source: Nanoscale Materials in Chemistry, Wiley, 2001

- If a bulk metal is made thinner and thinner, until the electrons can move only in two dimensions (instead of 3), then it is “2D quantum confinement.”
- Next level is ‘quantum wire
- Ultimately ‘quantum dot’

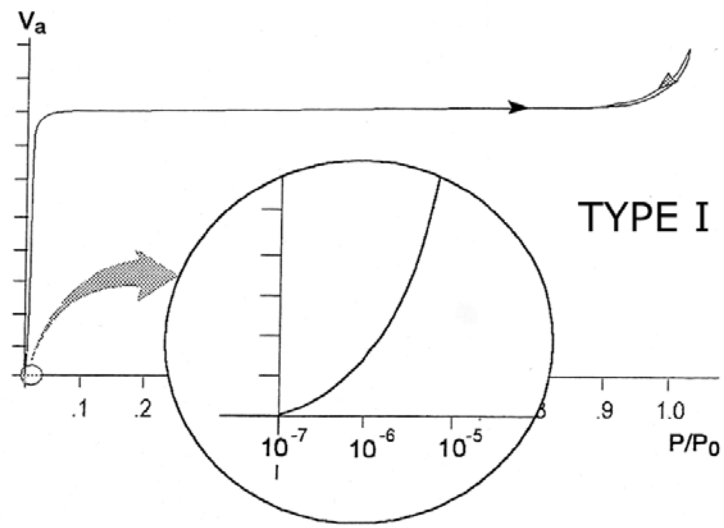
Adsorption

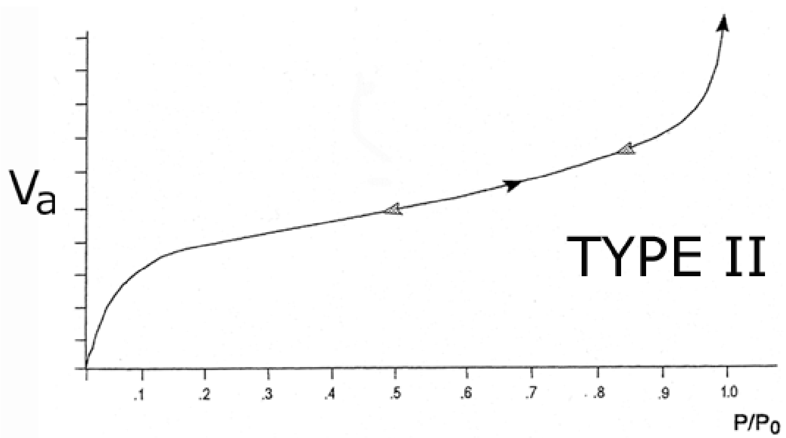
Adsorption: Some Background

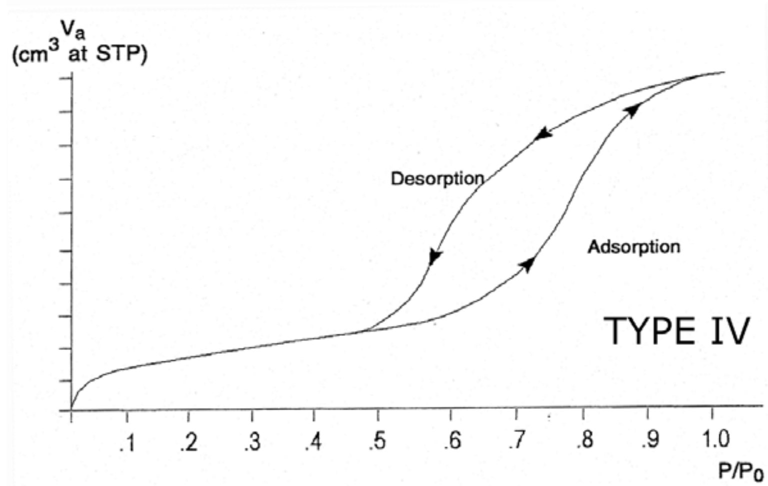
- Adsorption is like absorption except the adsorbed material is held near the surface rather than inside
- Bulk solids, all molecules are surrounded by and bound to neighboring atoms and forces are in balance. Surface atoms are bound only on one side, leaving unbalanced atomic and molecular forces on the surface. These forces attract gases and molecules $\Rightarrow$ Van der Waals force, $\Rightarrow$ physical adsorption or physisorption
- At high temperatures, unbalanced surface forces may be satisfied by electron sharing or valence bonding with gas atoms $\Rightarrow$ chemical adsorption or chemisorption
  - Basis for hetergeneous catalysis (key to production of fertilizers, pharmaceuticals, synthetic fibers, solvents, surfactants, gasolines, other fuels, automobile catalytic converters…)
  - High specific surface area (area per unit mass)

Physisorption

- Physisorption of gases by solids increases with decreasing T and with increasing P
- Weak interaction forces; low heats of adsorption < 80 KJ/mole; physisorption does not affect the structure or texture of the absorbent
- Desorption takes place as conditions are reversed
- Mostly, testing is done at LN_2 temperature (77.5 K at 1 atm.). Plot of gas adsorbed as volume V_a at 0° C and 1 atm (STP) vs. P/P_o (P_o is vapor pressure) is called adsorption isotherm.







Chemisorption

- Much stronger interaction than physisorption
- Heat of adsorption up to 800 KJ/mole
- Adsorbing gas or vapor molecule splits into atoms, radicals or ions which form a chemical bond with the adsorption site. $\Rightarrow$ Sharing of electrons between the gas and solid surface; may be regarded as the formation of a surface compound.
- Simple reversal is not possible like in physisorption
  - O_2 chemisorbed on charcoal $\Rightarrow$ application of heat and vacuum will result in CO desorption instead of O_2.
- Under favorable T & P, physisorption takes place on all surfaces. But chemisorption is localized and occurs on only certain surface sites
- Physisorption $\uparrow$ with $\downarrow$ in T; chemisorption $\uparrow$ with $\uparrow$ in T
- Same surface can exhibit physiosorption at low T and chemisorption at high T. Example: N_2 chemisorption on Fe at 800° C to form iron nitride but physisorption at LN_2 temperatures.

Chemisorption: Langmuir Theory

- Assumes gases form only one monolayer on a solid
- Gas molecule collision with solid ⇒ inelastic, so the gas molecule stays in contact with solid, for a time before desorbing
- Writing a balance between the rate at which molecules strike the surface and rate at which they leave:

$$V_a = \frac{V_m bP}{1 + bP}$$

V_m= quantity of gas absorbed when the entire surface is covered with a monolayer

- Rearranging, $\dfrac{P}{V_a} = \dfrac{I}{V_m b} + \dfrac{P}{V_m}$
- Plot of $\dfrac{P}{V_a}$ vs. P should yield a straight line if the equation applies ⇒ evaluate V_m and b
- Specific surface area $s = \dfrac{V_m \sigma N_A}{m V_0}$

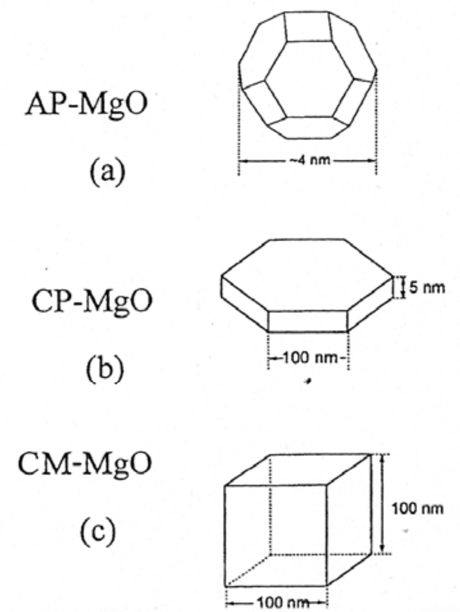
V_m= molar volume of the gas (22414 cm^3); N_A = Avog. #

σ = surface area occupied by single adorbed molecule, 16.2 A^2 for N_2

m = mass of the adsorbing sample

Nanomaterials in Catalysis

- Surface chemistry is important in catalysis. Nanostructured materials have some advantages:
  - Huge surface area, high proportion of atoms on the surface
  - Enhanced intrinsic chemical activity as size gets smaller which is likely due to changes in crystal shape
  - Ex: When the shape changes from cubic to polyhedral, the number of edges and corner sites goes up significantly
  - As crystal size gets smaller, anion/cation vacancies can increase, thus affecting surface energy; also surface atoms can be distorted in their bonding patterns
  - Enhanced solubility, sintering at lower T, more adsorptive capacity



Models of (a) nanocrystalline (AP-MgO); (b) microcrystalline (CP-MgO); (c) normal commercially available (CM-MgO) magnesium oxide crystals. Reprinted with permission from *Clusters & Nanostructure Interfaces*, **1999**, p. 578, World Scientific Publishing Co Pte Ltd.[1b]

Nanoporous Materials

- Zeolite is an old example which has been around a long time and used by petroleum industry as catalysts
- The surface area of a solid increases when it becomes nanoporous; this improves catalyst effects, adsorption properties
- ‘Adsorption’ is like ‘absorption’ except the absorbed material is held near the surface rather than inside
- How to make nanopores?
  - lithography followed by etching
  - ion beam etching/milling
  - electrochemical techniques
  - sol-gel techniques

Fine Particle Technology

- Frequently encountered powders:
  - Cement, fertilizer, face powder, table salt, sugar, detergents, coffee creamer, baking soda…

- Some products in which powder incorporation is not obvious
  - Paint, tooth paste, lipstick, mascara, chewing gum, magnetic recording media, slick magazine covers, floor coverings, automobile tires…

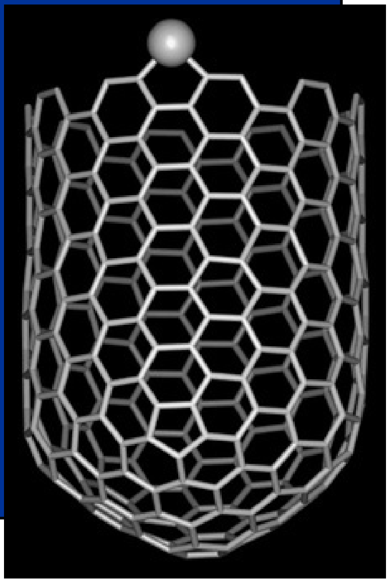
- For most applications, there is an optimum particle size
  - Taste of peanut butter affected by particle size
  - Extremely fine amorphous silica is added to control the ketchup flow
  - Medical tablets dissolve in our system at a rate controlled by particle size
  - Pigment size controls the saturation and brilliance of paints
  - Effectiveness of odor removers controlled by the surface area of adsorbents.

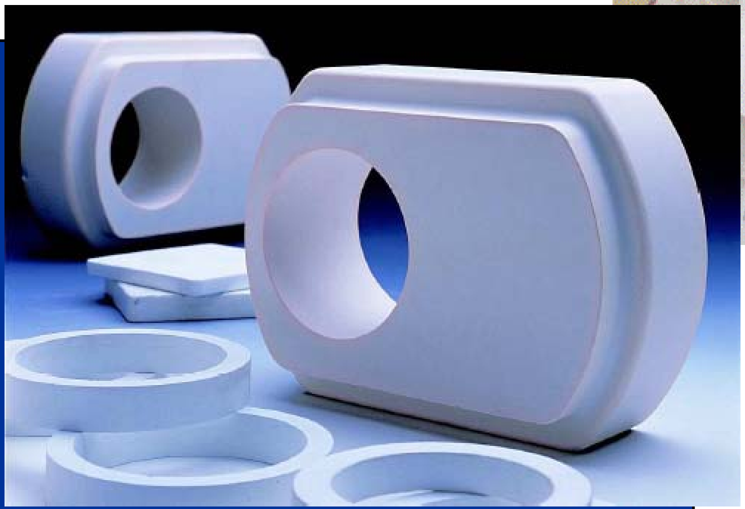
From: Analytical methods in Fine Particle Technology, Webb and Orr

- Ability to synthesize nanoscale building blocks with control on size, composition etc. → further assembling into larger structures with designed properties will revolutionize materials manufacturing
  - Manufacturing metals, ceramics, polymers, etc. at exact shapes without machining
  - Lighter, stronger and programmable materials
  - Lower failure rates and reduced life-cycle costs
  - Bio-inspired materials
  - Multifunctional, adaptive materials
  - Self-healing materials

- Challenges ahead
  - Synthesis, large scale processing
  - Making useful, viable composites
  - Multiscale models with predictive capability
  - Analytical instrumentation

- Carbon Nanotubes
- Nanostructured Polymers
- Optical fiber preforms through sol-gel processing of nanoparticles
- Nanoparticles in imaging systems
- Nanostructured coatings
- Ceramic Nanoparticles for netshapes





Source: IWGN Report

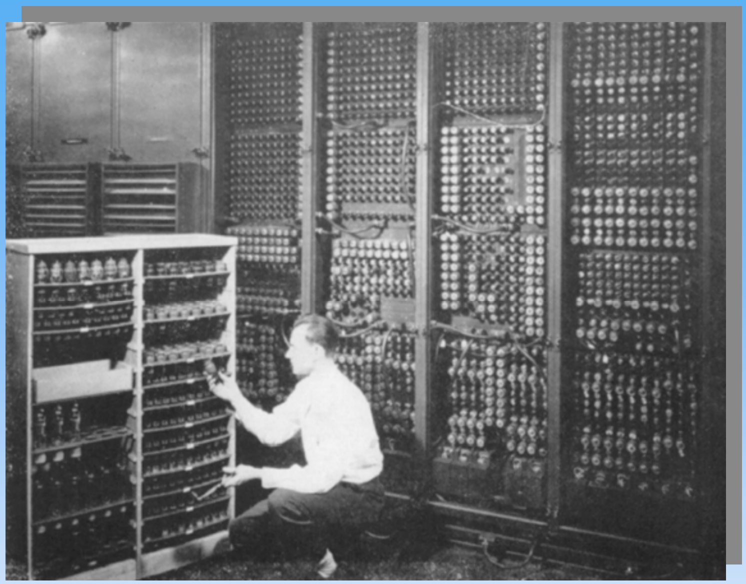
More Examples of Nanotech in Materials and Manufacturing

- Nanostructured metals, ceramics at exact shapes without machining
- Improved color printing through better inks and dyes with nanoparticles
- Membranes and filters
- Coatings and paints (nanoparticles)
- Abrasives (using nanoparticles)
- Lubricants
- Composites (high strength, light weight)
- Catalysts
- Insulators

Nanoelectronics and Computing

Past

Shared computing → thousands of people sharing a mainframe computer



Present

Personal computing

Future

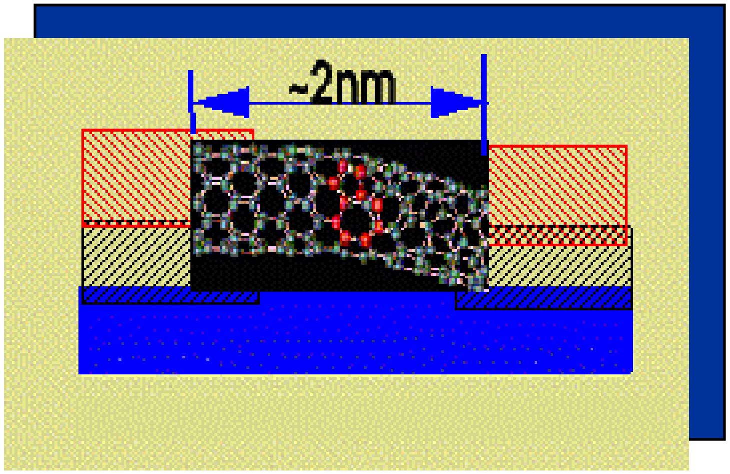
Ubiquitous computing → thousands of computers sharing each and everyone of us; computers embedded in walls, chairs, clothing, light switches, cars….; characterized by the connection of things in the world with computation.

- Quantum Computing
  - Takes advantage of quantum mechanics instead of being limited by it
  - Digital bit stores info. in the form of ‘0’ and ‘1’; qubit may be in a superposition state of ‘0’ and ‘1’ representing both values *simultaneously* until a measurement is made
  - A sequence of N digital bits can represent *one* number between 0 and 2^N-1; N qubits can represent *all* 2^N numbers simultaneously

1938	1998
Technology engine: Vacuum tube	**Technology engine: CMOS FET**
Proposed improvement: Solid state switch	**Proposed improvement: Quantum state switch**
Fundamental research: Materials purity	**Fundamental research: Materials size/shape**

- Stan Williams

- Carbon nanotube transistors by several groups
- Molecular electronics: Fabrication of logic gates from molecular switches using rotaxane molecules
- Defect tolerant architecture, TERAMAC computer by HP → architectural solution to the problem of defects in future molecular electronics



- DNA microchip arrays using advances for IC industry
- ‘Gene gun’ that uses nanoparticles to deliver genetic material to target cells
- Semiconductor nanocrystals as fluorescent biological labels

Source: IWGN Report

Summary

- Nanotechnology is not about simply shrinking the dimensions to 1- 100 nm level nor is the routine top-down miniaturization as we do in silicon CMOS fabrication. If that is the case, we do not need new terminologies and funding to continue the old stuff.

- Instead, it is about exploring novel properties that arise because of the nanoscale - properties that differ from their bulk counterparts.

- Once we identify such properties, the next big question is: What useful things can we do with that?

- There are several areas in which researchers have been able to answer positively to this question, leading to the evolution of the field.